Parasitic Reactions in MOVPE Growth of AlGaN: Experiment and Modelling

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Introduction

$Al_xGa_{1-x}N$ is a crucial component in most group III-nitride based devices. It is used as an electron barrier in light-emitting diodes and lasers ($x \approx 15\,\%$) [1], serves as a cladding material in lasers ($x \approx 8\,\%$) [1], and is employed as a material for heterostructures of FETs (x up to $100\,\%$) [2]. Therefore, a wide range of Al-content has to be realized by epitaxial growth to fulfill device requirements.

A major problem for metalorganic vapor phase epitaxy (MOVPE) growth of AlGaN are parasitic reactions in the reactors gas phase. These premature reactions can be reduced with lower growth pressures [3]. In our study we show the dependence of the Al-content on fluxes and pressure. Furthermore we derive a model for quantitative prediction based on collision theory.

Experimental

For our growth experiments we used an Aixtron AIX 200 RF horizontal MOVPE reactor. On c-plane sapphire we grew structures consisting of a $2\,\mu$m GaN buffer and AlGaN layer ($100 - 300$ nm) at $1030\,°$C. AlGaN layers were grown at reactor pressures ranging from 25 to 220 mbar and molecular TMAl/TMGa ratios from 0.28 to 4.

The Al-content was derived mostly from X-ray diffraction measurements ((0002)-reflex in $\omega - 2\Theta$-scans). Samples with a microscopically (magnification $\geq$100) visible cross hatch pattern are treated as relaxed material for the determination of Al-content using Vegard's law. Additionally, in some cases the Al-content was determined by in situ reflectance measurements from the increase in growth rate when TMAl was added to the gas phase.

Results and Discussion

For epitaxial growth the relation between the composition in the supplied gas phase and the resulting solid state composition is decisive. So we compare the ratio of TMAl to TMGa molecules injected into the gas phase (r_{gp}) with the obtained ratio of Al to Ga in the solid state $Al_xGa_{1-x}N$ ($r_{ss} = x/(1-x)$). Without prereactions in the gas phase the ratio of solid state composition to gas phase composition r_{ss}/r_{gp} would be given by the ratio of incorporation efficiencies of Al (i_{Al}) to Ga (i_{Ga}):

$$\frac{r_{ss}}{r_{gp}} = \frac{i_{Al}}{i_{Ga}} \tag{1}$$

In Fig 1. r_{ss}/r_{gp} is plotted versus the growth pressure (p) for different injection ratios r_{gp}.

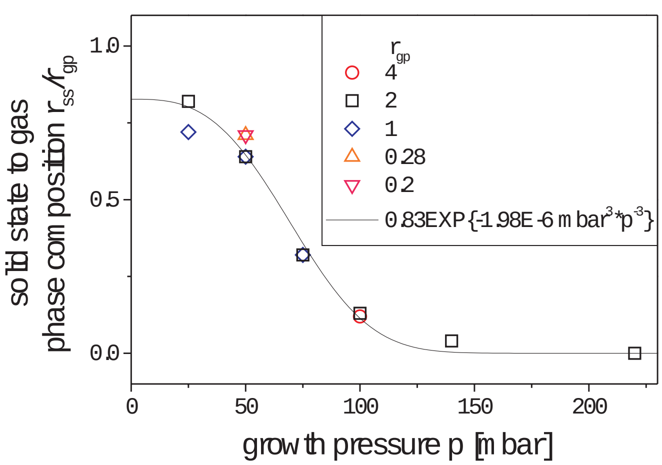

Figure 1: Pressure dependence of solid state to gas phase composition ratio r_{ss}/r_{gp} for different gas phase compositions r_{gp}, the solid line represents a two parameter fit according to eq. 5

We find a strong decrease of r_{ss}/r_{gp} with increased pressure, which means that with higher reactor pressure the aluminum content of the structure is reduced. This relation is independent of the gas phase ratio.

We propose this behavior is caused by a homogeneous gas phase reaction between ammonia and TMAl (cf. [4]). Reactions with TMGa are negligible. After mixing hydrides and metal organics the TMAl concentration in the gas phase is reduced on the way towards the sample, yielding a reduced ratio r'_{gp} in the growth region. With the excess of NH_3 compared to TMAl we presume a first order reaction, leading to a time dependence according to

$$r'_{gp} = r_{gp} e^{-\alpha t}, \tag{2}$$

where the reaction constant α, depending on pressure, temperature, V/III ratio, etc., describes the amount of effective collisions between TMAl and NH_3. From the ideal gas we take $\alpha \propto p^2$ as the number of reactions per times is proportional to the number of collisions per time given by the volume collision rate proportional to p^2 [5]. The time for a volume in the gas phase to travel from reactor inlet to substrate is proportional to the growth pressure ($t \propto p$). This results in

$$r'_{gp} = r_{gp} e^{-\alpha' p^3}. \tag{3}$$

As the solid state composition is determined by the gas phase composition at the growth zone r'_{gp} and the incorporation efficiencies, this yields

$$r_{ss} = \frac{i_{Al}}{i_{Ga}} r'_{gp} = \frac{i_{Al}}{i_{Ga}} r_{gp} e^{-\alpha' p^3}. \tag{4}$$

In Fig. 1. we displayed

$$\frac{r_{ss}}{r_{gp}} = \frac{i_{Al}}{i_{Ga}} e^{-\alpha' p^3}. \tag{5}$$

At p =0 mbar, where prereactions are negligible, a value for i_{Al}/i_{Ga} can be obtained. Describing the data in Fig. 1 with Eq. (5), we obtain i_{Al}/i_{Ga}=0.83, a lower incorporation of Al in respect to Ga. For α' we get $1.98 \cdot 10^{-6}\,\mathrm{mbar}^{-3}$, a value accounting for effective reaction cross section, reactor constants, distance from mixture to substrate, etc. The overall agreement of the experimental data to the deduced formula is quite good.

Based upon the reasonable assumption of homogenous parasitic reactions between ammonia and TMAl we were able to develop a simple yet powerful model for the growth of AlGaN. It enables quantitative predictions in a wide pressure and gas phase composition range. Beyond this we find a different incorporation efficiency for Al and Ga (i_{Al}/i_{Ga}=0.83).

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